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(54) Method for imparting water repellency to leathers from animal skins

(57) The method for imparting water repellency to leathers from animal skins, in particular suede and nubuck leathers made from pigskin, is used in operations which manufacture, for example, leather for shoe uppers and boot leather for fall and winter weather footwear or leather for outerwear. The object of the invention is to provide shoe and clothing manufacturers with materials from which essentially waterproof footwear and outerwear may be produced. The essence of the invention consists in stuffing the leather with substance mixtures, coordinated for waterproofness, composed of oxidized, low-sulfated aliphatic hydrocarbons and alkyl sulfates in ratios between 1 to 0.5 and 1 to 3, and impregnation with solutions and/or suspensions of chemical compounds in which bivalent and/or multivalent metal ions and octadecenoic acid radicals are bound by complexing or ionic bonding. The octadecenoic acid radicals may be reacted alone and/or with acid radicals of higher carbonic acids.

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Description of the Invention**Title of the invention**

Method for imparting water repellency to leathers from animal skins

Field of application of the invention

The invention is used in operations which prepare leathers from animal skins, in particular suede and nubuck leathers, imparted with the highest possible water repellency, for example leather for shoe uppers and boot leather for fall and winter weather footwear, and leather for outerwear.

Characteristics of the known technical approaches

The preparation of water-repellent leather from animal skins has a history as old as leather preparation itself, since leather from animal skins is not inherently water-repellent. In particular suede and nubuck leathers prepared according to current methods have pronounced water absorbency, resulting in rapid water penetration when exposed to wet weather conditions and in test equipment. For suede and nubuck leathers made from pigskin, this use-impairing characteristic is intensified by hair follicles which extend through the entire leather skin. There is a long and abundant history of attempts to impart water repellency to suede and nubuck leathers.

A distinction is made between

- products that may be used in organic solvents and
- agents used in aqueous media.

Chemical products that may be used in organic solvents are essentially the following:

- fluorine-containing chemicals,
- silicone-based products,
- high molecular weight fatty acid esters, and
- organometallic paraffin compounds.

Chemical agents used in aqueous media are essentially the following:

[Illegible]

- metal stearic acid complexes,
- metal salt-containing emulsions of high molecular weight hydrocarbons,
- water-soluble fluorine-containing chemicals, and
- high molecular weight fatty acids, in particular stearic acid and its salts.

The water-repellent effect is evaluated, among other methods, by determining the water penetration in the penetrometer, the percentage of water absorption after two hours' compression in saline solutions, and the wettability of the surface over a period of minutes.

Imparting water-repellency to leathers has effects on the touch, flexural strength, coloration, rub-fastness, washability, and cleaning resistance.

S.L. Ivaskevic, M.P. Kotov, and N.S. Sorokin reported on a 45% reduction in water absorption by use of organosilicon compounds. H.F. Lee treated chrome-tanned leather with long-chain dicarboxylic acid salts, followed by treatment with ammonia.

K. Boroyan has defined three principles of hydrophobization:

1. Filling the interfibrillary interstices with fat, oil, wax, or prepolymer, among other materials;
2. Treating the leather fibers with water-repellent agents, such as silicone compounds;
3. Treating with hydrophilic compounds such as alkoxy succinic acid, which upon initial contact with water forms stable emulsions and thus prevents further penetration of water.

R. Radzynkiewicz tested silicone products from Poland, United Kingdom, and France, and fluoroorganic products from the Federal Republic of Germany.

A. Simoncini and G. Manzo obtained water-repellent chrome-tanned leather by treating the leather with a trimethylated dicarboxylic acid containing six C atoms and an unsaturated monocarboxylic acid containing 18 C atoms, with the addition of glutardialdehyde and chrome tanning agent.

R.P. Seibert described the hydrophobization with silicones in a solvent system and in the aqueous phase.

K.A. Drijanow, V.L. Sidorov, and P.I. Levenko reacted chrome-tanned leather

with organic silicon compounds and crosslinking amines with the addition of 20% tetrabutoxytitanium.

K.M. Zurabjan, V.V. Nepomina, and K.S. Puscevaja sprayed mixtures of silasanes and siloxanes and solutions thereof in toluene or butyl acetate on air-dried leather and leather containing 30% moisture.

S.L. Ivaskevic, S.C. Ponomatow, and K.S. Puscevaja sprayed leather with solutions of polymethylsilasane and polymethoxysiloxane with tetrabutoxytitanium as catalyst, and dried same at 50°C.

R. Widder achieved simultaneous hydrophobization and stuffing of leather by the use of acetoacetates, diamines, and mono- or dialdehydes in conjunction with emulsifiers.

A. Blazej, A. Galatik, and A. Müllerova achieved hydrophobization by neutralizing with ammonia, impregnating with alkaline fatty acid salts, and fixing with chromium salts.

R. Nowak sought water-repellent leather having low wetting agent and chromium oxide requirements. He treated leather with high molecular weight polycarbonic acids and encapsulated silicone products, fatty acid esters, and zirconium complex compounds with paraffin.

Z. Virpsza and Z. Klimala sprayed hydroxymethylstearic acid amide and stearyl amidotoluene monoisocyanate in chloroform on cowhide suede.

K.M. Zurabjan, B.V. Nepomina, and L.V. Svobodskij considered the use of organic silicon compounds with and without functional groups to be the most suitable for hydrophobization when tetrabutoxytitanium was used as catalyst.

J. Just, S. Popp, and R. Müller used Densodrin from BASF, fixation with 60% basic chrome tanning agent, and treatment with quebracho wood extract and mimorarinene extract to hydrophobize cowhide leather. Similar results were obtained using stearic acid-chromium complexes and suspension-stretching frame drying.

C.E. Retzsch treated chrome-tanned leather with polymeric phosphate esters containing alkoxyated and phosphatized alkylphenol-polyphenol condensates, followed by stuffing with a hydrophobic stuffing agent which had been mixed with an amine-neutralized fatty alcohol phosphate.

J.M. Schuster and M.H. Olson achieved water repellency of anionically charged collagen fiber matrices by treatment with a water-soluble chromium complex of substituted and unsubstituted alkanic acids, and simultaneous or subsequent

treatment with a carbodiimide also containing fluoroaliphatic radicals or fluoroaliphatic side chains.

H. Träubel, K. Pisaric, and H. Strenger impregnated flat protein-based structures with water-emulsified solvent-free compounds containing isocyanate groups, together with a softener.

R. Heyden and A. Asbek prepared water-repellent leather by processing a mixture of acidic citric acid esters of a fatty alcohol having a chain length of C_{12} to C_{22} with a water-soluble organic solvent having a boiling point above 100°C and which dissolves the citric acid ester.

F.C. Saunders and C.B. Smith prepared leather with long-lasting water repellency by treating with titanium and zirconium compounds of the general formula $\text{Ti}(\text{OR})_4$ and $\text{Zr}(\text{OR})_4$, where R represents an aliphatic residue containing fewer than 13 C atoms and fewer than 4 OH groups, with methylpolysiloxanes and with polysiloxanes in organic solvents.

Object of the invention

The object of the invention is to provide clothing and shoe manufacturers with leather having long-lasting water repellency for clothing and for shoe and boot uppers, such that, with appropriate processing, essentially waterproof footwear and outerwear, even under wet fall and winter weather conditions, may be offered to end users. The preparation is implemented using materials produced within the German Democratic Republic.

Description of the essence of the invention

The preparation of stylish leather footwear and clothing, in particular made of suede and nubuck leathers, does not inherently result in the imparting of water repellency.

Over time, continually increasing demands for consistency and fashionableness of aniline dyes, elegant finishing of leather, and economical leather preparation have resulted in the use of various types of surfactants and multiple processing steps for leather. In order to use stuffing agents and dyes in the aqueous phase, i.e., in an economical manner, these materials have been highly sulfated, sulfited, or sulfonated, or have been made water-soluble, emulsifiable, and/or suspendable by chemical manufacturers. Synthetic tanning agents and dye-

leveling agents as well as finishing agents inherently contain in their molecular structures chemical substituents which result in good water solubility.

As a result, however, stylish, elegant leather, in particular velour and nubuck leathers, have become highly water-absorbent. For pigskin leathers, this tendency has been facilitated by the hair follicles which penetrate the entire leather skin. The reduction in usefulness has resulted in numerous efforts to partially or completely eliminate this shortcoming. The number of substances that have been developed, and methods that have been published, is substantial. Understandably, chemical manufacturers have already identified and marketed hydrophobicizing products which have a very slight, barely discernible hydrophobicizing effect when applied to a normally treated, i.e., very water-absorbent, leather. The problem of measuring waterproofness is addressed in the German Democratic Republic by testing in the penetrometer with compression to the point of initial water penetration, and standardizing to the percentage of water absorption following compression for two hours.

Satisfactory preparation of waterproof pigskin suede leather has heretofore not been possible in this country.

The method according to the invention provides leather which survives compression for 9 hours in the penetrometer in 0.5% saline solution, corresponding to 27,000 compressions. After compression for two hours, the water absorption by the leather was less than 12%. Leather imparted with such long-lasting water repellency, in particular nubuck and suede leathers made from pigskin, has been commercially prepared only in small quantities. The essence of the invention lies in coordinating the quantity and quality of the pretreatment, stuffing, and impregnation of the leather with the materials to be used according to the invention in a targeted manner with respect to long-lasting water repellency.

It should be noted that hydrophobicizing stuffing agents, such as the partially oxidized, low-sulfated aliphatic hydrocarbons having a chain length of C_{15} to C_{40} , when used alone have a pronounced ability to absorb onto the leather surface, yet are not very able to penetrate into the interior of the leather. Sole use of the hydrophobicized stuffing agent thus results in excessive surface oiliness,

greasiness, and brittle hardness of the leather, since softness is imparted by stuffing agents which are incorporated inside the leather, and also results in a low water-repellent effect, since the stuffing agent adhering to the surface is mechanically removed after a short time. For this reason, fat-distributing substances should also be used which facilitate penetration of the hydrophobicizing stuffing agent into the interior of the leather substance without significantly impairing the water-repellent effect thereof.

According to the invention, alkyl sulfates having alkyl radicals with chain lengths of 15 to 40 carbon atoms, preferably 18 to 25 carbon atoms, are suited for this purpose, specifically, in a proportion of at least 50% of the quantity of the hydrophobicizing stuffing agent used, up to approximately 300%, and not—as has been described in textbooks on leather preparation or in reports from manufacturers of leather stuffing agents and auxiliary agents—up to a maximum 10% of the hydrophobicizing stuffing agent used.

Depending on the compactness of the leather material, thickness of the leather, softness to be achieved, surface appearance, desired degree of waterproofness, and processing technology in the footwear and clothing industries, the ratio of hydrophobicizing stuffing agents to fat-distributing substance is variable. In practice, the quantities of substance mixture used are not less than 2% and not greater than 15%, relative to the wet-split and/or wet-folded leather stock.

The uniformity of the fat distribution in the leather may be monitored and controlled by analytical layer tests.

Even if a reduction in water absorbency in the leather can be established as the result of uniform distribution in the leather of partially oxidized and low-sulfated aliphatic hydrocarbons having chain lengths of 15 to 40 carbon atoms, to achieve a particularly long-lasting water-repellent effect it is necessary in a separate procedure according to the invention to impregnate with compounds in which bivalent and/or multivalent metal ions and octadecenoic acid radicals are bound by complexing or ionic bonding.

These compounds may be used in the form of true and/or colloidal solutions or suspensions. Depending on the degree of desired waterproofness, softness, and surface quality of the leather, 0.25 to 6 moles octadecenoic acid should be bound

with a bivalent and/or multivalent metal atom. Chemical bonding of bivalent and/or multivalent metal ions with octadecenoic acid radicals may be used for impregnation, alone and/or in a mixture with chemical compounds of bivalent and/or multivalent metal ions with acid radicals of higher carbonic acids such as decanoic, hexadecanoic, octadecenoic, or octatridecenoic acid. Since octadecenoic acid occurs in esterified form with glycerin in natural fats together with other carbonic acids, chemical compounds of bivalent and/or multivalent metal ions with mixtures of carbonic acid radicals occurring in esterified form with glycerin in qualitative and quantitative composition in natural fats such as rapeseed oil, linseed oil, or lard are consequently used for impregnation of leather.

The quantities used, depending on the required or necessary degree of waterproofness, softness, and surface quality of the leather, are 1% to 15% of a 10% to 35% solution or suspension of the impregnating agent or impregnating agent mixture according to the invention, relative to the dry mass of the leather, and/or 0.5% to 10% of a 10% to 35% solution or suspension of the impregnating agent or impregnating agent mixture according to the invention, relative to wet-split and/or wet-folded leather stock.

It is noted that the impregnation according to the invention with chemical compounds of bivalent and/or multivalent metal ions with octadecenoic acid radicals of any given leathers, usually stuffed leathers, causes a certain hydrophobicizing effect such that waterproofness of the leather, lasting for several hours, can be reliably achieved in test equipment and while wearing shoes and clothing articles made therefrom only in combination with stuffing of the leather with the substance mixtures according to the invention composed of oxidized and low-sulfated aliphatic hydrocarbons and alkyl sulfates.

The method for imparting water repellency to leather may be used in all conventional vessels for leather preparation, and employing all facilities installed in leather manufacturing plants, under the customary conditions for reaction temperatures, reaction times, quantities of reaction baths, and pH values.

Exemplary Embodiment

The example is intended to illustrate the invention without limiting the invention thereto.

Preparation of a waterproof pigskin suede leather having a thickness of 1.4 to 1.6 mm

Pigskins which were adequately degreased by mechanical means, softened without addition of emulsifiers, chemically degreased with minimum addition of emulsifiers, dehaired according to customary methods, and limed, delimed, bated, pickled, and tanned without the addition of emulsifiers but according to customary methods, were brought to a leather thickness of 1.9 mm after lowering the acid content and mechanical dewatering, neutralized in vessels conventionally used in leather preparation, and stuffed as follows:

The washed or rinsed leather was agitated in a 50% to 200% aqueous reaction bath, relative to a wet-split leather stock. The reaction temperature was 50°C to 65°C. Outside the reaction vessel a 5% stuffing agent, relative to a wet-split leather stock, and composed of up to approximately 85% oxidized, low-sulfated aliphatic hydrocarbons was used to prepare an aqueous emulsion at 60°C, and a 5% alkyl sulfate, relative to a wet-split leather stock, was used to prepare an aqueous solution at 60°C. The emulsion and solution were added simultaneously or in rapid succession to the agitated reaction vessel containing the leather. The reaction time was 1 to 8 hours, depending on the results of the analytical layer test for fat distribution. The leather thus stuffed was then washed, and, if necessary, the smoothness was reduced by use of synthetic tanning agent or other agents.

After dewatering, milling, afterdrying, and possible thickness correction, the grain layer was split at a thickness of 0.1 to 0.2 mm, and the leather was abraded with coarse sandpaper coated with corundum or silicon carbide grit on the layer from which the grain was split in the preceding operation. After dedusting, the leather was softened in vessels customarily used in leather preparation without the addition of emulsifier, dyed with water-soluble aniline dyes, and, if necessary, auxiliary dyeing agents, fixed, and impregnated as follows:

The washed or rinsed leather was agitated in a 500% aqueous reaction bath, relative to the mass of the dry leather, and adjusted to a pH of 2.5 to 2.7 by use of organic acids. At a reaction temperature of 30°C, 10%, relative to the mass of the dry leather, of the 25% alcoholic solution of a complexed chromium (III) salt of octadecenoic acid was added undiluted to the agitated reaction vessel. The reaction time was 1 to 3 hours. The acid added for pH adjustment was then substantially neutralized by use of a mild alkali. The leather was washed, intensely predried as much as possible in a suspension dryer, and finished according to customary methods.

Claims

1. Method for imparting water repellency to leathers from animal skins, in particular suede and nubuck leathers made from pigskin, which have been adequately mechanically degreased and fleshed, softened without addition of emulsifiers, chemically degreased with minimum addition of emulsifiers, and dehaired, limed, delimed, enzymatically treated, pickled, tanned and dyed according to customary methods but without the addition of emulsifiers, characterized in that degreasing is performed using substance mixtures, mutually coordinated for waterproofness, composed of oxidized, low-sulfated aliphatic hydrocarbons and alkyl sulfates, and impregnation is performed using true or colloidal solutions and/or suspensions of chemical compounds in which bivalent and/or multivalent metal ions and octadecenoic acid are bound by complexing or ionic bonding.
2. Method according to Claim 1, characterized in that, depending on the required or necessary degree of waterproofness, softness, and surface quality of the leather, the oxidized, low-sulfated aliphatic hydrocarbons are mixed with the alkyl sulfates in ratios between 1 to 0.5 and 1 to 3.
3. Method according to Claim 2, characterized in that the mixture is prepared in the form of aqueous solutions or emulsions inside and/or outside the reaction vessel and/or the leather preparation facility.
4. Method according to Claim 2, characterized in that the oxidized, low-sulfated aliphatic hydrocarbons have chain lengths of 15 to 40 carbon atoms, preferably 21 to 32 carbon atoms.
5. Method according to Claim 2, characterized in that the alkyl radicals of the alkyl sulfates have chain lengths of 15 to 40 carbon atoms, preferably 18 to 25 carbon atoms.
6. Method according to Claim 2, characterized in that the substance mixture is used in quantities of 2% to 15%, relative to the wet-split and/or wet-folded leather stock, after the chrome tanning.

7. Method according to Claim 1, characterized in that, depending on the required or necessary degree of waterproofness, softness, and surface quality, a bivalent and/or multivalent metal ion is chemically bound to 0.25 to 6 moles octadecenoic acid radicals.
8. Method according to Claim 7, characterized in that chemical bonding of bivalent and/or multivalent metal ions with octadecenoic acid radicals is used, alone and/or in a mixture with chemical compounds of bivalent and/or multivalent metal ions with acid radicals of higher carbonic acids such as decanoic, hexadecanoic, octadecenoic, or octatridecenoic acid, for impregnation of the leather.
9. Method according to Claim 7, characterized in that chemical compounds of bivalent and/or multivalent metal ions with mixtures of acid radicals of higher carbonic acids occurring in qualitative and quantitative composition in natural fats, such as rapeseed oil, linseed oil, or lard, esterified with propanetriol are used for impregnation of the leather.
10. Method according to Claim 7, characterized in that the quantities of the 10% to 35% solutions or suspensions of chemical compounds of bivalent and/or multivalent metal ions with octadecenoic acid radicals used alone and/or in a mixture according to Claims 8 and 9, depending on the required or necessary degree of waterproofness, softness, and surface quality, are 0.5% to 10% relative to the wet-split and/or wet-folded leather stock, after chrome tanning, and/or 1% to 15% relative to the dry mass of the leather.